EVIDENCE FOR LONG-CHAIN ALIPHATIC STRUCTURES IN SPORINITE
KEROGEN BY ALAKALINE POTASSIUM PERMANGANATE OXIDATION

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INTRODUCTION

Microscopical examinations of kerogens have shown that many coal macerals are not restricted to coal swamp depositional environments, but are in fact widespread in occurrence, in many types of sedimentary rocks. Exinites in particular are of geochemical interest, for they have been implicated in crude oil generation under certain circumstances[1-3]. They are also common components of coals of diverse ages[4]. The work reported here represents a part of a study undertaken to compare chemical similarities and differences between different macerals[5] and outlines the results of oxidative degradation of a series of sporinite concentrates isolated from Carboniferous coals of high-volatile bituminous rank.

SAMPLES AND ANALYTICAL METHODS

A series of sporinite concentrates were prepared from selected coals by a combined crushing, heavy liquid ($ZnCl_2$) flotation technique, modified after the method of Dormans et al[6]. Final concentrate purities ranged from 77-95% of sporinite, with the main contaminants being inertinites. The samples cover the rank range 0.5-1.1%$\overline{R}_{max}$ (equivalent to vitrinite carbon contents of 77-87%). Prior to oxidation, all samples were extracted with a chloroform: acetone: methanol mixture (47:30:23 v/v) and then saponified with a solution of KOH in methanol (5% w/v).

The oxidation procedure was taken from the kerogen oxidation method of Djuricic et al[7], whereby the sporinite was dispersed in an excess of 1.6% KOH solution at 80°C and an aliquot of potassium permanganate was added (the ratio of sporinite: oxidant varied between 4:1 and 1:1 in different experiments). After consumption of the oxidant, the mixture was filtered, and residual sporinite was returned to the reaction vessel for a second oxidation step, this procedure being continually repeated until no further oxidation took place. Filtrates from each oxidation step were acidified to pH 1 and the resultant brown to black precipitates were removed. Residual solutions were extracted with diethyl ether to recover organic-soluble acid fractions, which were then methylated with diazomethane. The esters were fractionated by preparative thin-layer chromatography (0.5 mm SiO_2 plates, developed in petroleum ether: ether 9:1), and resulting mono- and dimethyl ester fractions were analyzed by temperature-programmed gas chromatography.

RESULTS AND DISCUSSION

Pertinent data concerning the samples and oxidation products are given in Table 1.

TABLE 1

Rank and Oxidation Product Data for Sporinite Kerogen

Sample	Rank $\bar{R}_{max}$ %	Oxidation Products Monobasic Acids (as Me esters) (ppm)	Dibasic Acids (as di-Me esters) (ppm)	Ratio Coal/Oxidant (w/w)	Number of Oxidation Steps
A	0.51	740	4060	4:1	13
B	0.60	640	15670	4:3	7
C	0.63	460	17970	1:1	6
D	0.68	720	21510	1:1	6
E	0.91	1160	12890	4:1	20
F	1.04	470	16080	1:1	7
G	1.12	610	16470	1:1	7

The distributions of straight-chain compounds in both the mono- and dibasic chromatographic fractions showed several progressive changes as the rank of the sporinites increased, and also as oxidation progressed within individual sporinites. Initial oxidation steps of low-rank sporinites (samples A-D) yielded complex mixtures of acids (range C_n-C_{28}) dominated by normal, saturated, even-carbon-numbered components with 14-20 carbon atoms. In later oxidation steps, normal acids became increasingly predominant and contained increasing proportions of long-chain (C_{20}) homologues, which eventually become the dominant products. The long-chain compounds showed a slight predominance of C_{22}, C_{24}, C_{26} and C_{28} acids. At ranks higher than 0.9% $\bar{R}_{max}$ (samples E-G), products were confined mainly to the range C_n-C_{18} with prominent straight-chain constituents, and the C_{18+} fraction was seen in trace amounts only.

The main aliphatic products in the dibasic chromatographic fraction were straight-chain, saturated α,ω-dicarboxylic acids in the range C_n-C_{28}, although homologues higher than C_{15} were always minor components and were confined to the lower rank samples. Individual compound concentrations decreased regularly with increasing chain length from maxima at C_8 or C_9. With increasing sample rank, the concentration of α,ω-dicarboxylic acids in the dibasic fraction decreased progressively, and at the highest ranks, virtually no recovery of these compounds was obtained.

The monobasic acids are produced by oxidative cleavage of an n-alkyl moiety bonded to the kerogen structure at one end of the chain. The nature of the function involved is unknown, except that esters are unlikely since all the samples were saponified prior to oxidation. The saponification procedure yielded low quantities of fatty acids (10 ppm) and n-fatty acids above n-C_{22} were not produced. No α,ω -dicarboxylic acids were produced[5]. Further, functional group analyses of coals indicate that carboxyl groups do not survive into the bituminous rank range[8]. The n-alkyl moieties exhibit some characteristics which indicate derivation directly from the original plant lipids. Long-chain (C_{20}) n-acids are probably derived from original plant waxes, which show a strong predominance of even-carbon-number chains in modern plants. Coalification processes have modified the original distribution so that the even-dominance has been almost smoothed out. Such a smoothing out process of original biolipids has been demonstrated many times in the solvent-soluble fractions of sedimentary organic matter, including coals[9-11]. The short-chain (C_{20}) n-acids have distributions indicating derivation from fats, particularly the predominance of n-C_{16} and n-C_{18}. These compounds are similar in distribution to simple alkyl degradation products of sporopollenin, a natural biopolymer found in modern exine walls[12], suggesting that this material may contribute to the structure of fossilized sporinite.

The α,ω -dicarboxylic acids are produced by diterminal oxidative cleavage of polymethylene chains within the kerogen. The nature of the original terminal structures is unknown, but alkylated mono- and diaromatic hydrocarbons bearing n-alkyl substituents of similar chain lengths have been observed in the pyrolysis products of some of these sporinites[13]. Poly-methylene chains have been found in a wide variety of sedimentary organic materials, frequently with chain lengths extending beyond C_{20}[14-17]. In an extreme case, the exinite maceral alginite (Botryococcus type) is composed of significant amounts of a highly cross-linked polymethylene chain network [18,19]. In the majority of published data, the distribution of chain lengths in the polymethylene structures does not suggest direct incorporation of simple lipids with the retention of original structures. Thus, it is thought that during the diagenetic alteration stage, the incorporation of functionalized lipids into a developing geopolymer takes place in such a way that biological identity is lost, possibly by chain fragmentation or cross-linking. Laboratory simulation of such a process has been carried out, whereby artificial melanoidins (representing polyfunctional proto-kerogen) have been reacted with standard alkenes, acids and alcohols (representing lipids)[20]. Data obtained to date suggest that a specific compound, for example n-hexadecanol, reacts with the melanoidin in a complex manner which produces an homologous series of chemically bonded alkyl moieties with chain lengths shorter than the original structure.

While the origin of the polymethylene structures is speculative, the oxidation data show that they are not stable under advancing coalification, and are progressively lost from the kerogen at successively higher ranks. The evidence further suggests that they are expelled as complete entities, for there is no good indication of progressive chain shortening with increasing rank.

SUMMARY

n-Alkyl moieties are present in at least two modes in sporinite kerogen, although they represent very small proportions of the total structure. Singly-bonded "peripheral" alkyl chains have been found, with chain length distributions which suggest direct incorporation of fats and waxes from the original plants. Coalification slowly modifies the structures so that specific biological identities are slowly obliterated. Diterminally bonded polymethylene chains are also present, and these structures are thought to develop during early diagenesis through complex reaction pathways involving functionalized lipids and poly-functional substrates.

The oxidation data suggest that oxidizable n-alkyl moieties are slowly expelled from the kerogen matrix, for recoveries decline as the rank of the sporinite increases. However, caution must be exercised in interpretating data from a single degradation technique, for pyrolytic degradation yielded significant quantities of n-alkanes from all the sporinite kerogens. Thus, it would appear that further n-alkyl moieties must be present, but incorporated in a manner which is not susceptible to alkaline permanganate oxidation.

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